Fabric Binder Lubricant

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(71) Applicant: 000003975
Nitto Boseki Co., Ltd.
1 Aza-Higashi, Gonome
Fukushima City, Fukushima Prefecture

(72) Inventor: J. Saito
2-2 Aza-Hino, Toyano
Fukushima City, Fukushima Prefecture

(72) Inventor: H. Inokuchi Hirokazu Inoguchi
57-9 Horai-cho
Fukushima City, Fukushima Prefecture

(54) [Title of the Invention]

SECONDARY SIZING AGENT FOR GLASS FIBER, AND GLASS CLOTH

(57) [Abstract]

[Object] To provide a warp secondary sizing agent for glass fiber, which provides weaving ability equivalent to that of a starch-based secondary sizing agent, in weaving glass fiber using a synthetic resin-based binder with no

need to remove the oil, and which can provide impregnability with the matrix resin of woven glass cloth and solder heat resistance for any formed laminates which are equivalent to or better than in the case of using glass cloth subjected to an oil removal process.

[Constitution] Warp secondary sizing agent for glass fiber consisting mainly of polyvinylpyrrolidone, and glass cloth in which said secondary sizing agent is used.

[Scope of the Patent Claim(s)]

[Claim 1] Warp secondary sizing agent for glass fiber, characterized in that it is composed mainly of polyvinylpyrrolidone.

[Claim 2] Glass cloth using the warp secondary sizing agent of Claim 1.

[Detailed Description of the Invention]

[0001]

[Field of Industrial Application] The invention pertains to a warp secondary sizing agent necessary when weaving glass cloth and, in particular, to a warp secondary sizing agent effective in weaving glass cloth that requires no thermal oil removal process.

[0002]

[Conventional Techniques] Glass cloth is generally woven from glass yarn treated with a binder such as a starch- or cellulose-based binder. In this case, warp secondary sizing agents based on starch and cellulose, and composed mainly of polyvinyl alcohol (PVA) are used. In the case of glass cloth using a starch-based binder, an oil removal process to remove the binder is required in order to improve the affinity of the cloth for the polyester resins, epoxy resins, and phenolic resins used as matrix resins. This oil removal process is usually carried out by heating, because the residual amount of binder must

be reduced to 0.1% or less. However, this oil removal process using heat has the following drawbacks:

(1) It degrades the performance of the glass fiber;

(2) It requires a high energy expenditure;

(3) It is a batch process and thus cannot be adapted to continuous operation.

[0003] As opposed to this, the manufacture of glass cloth requiring no oil removal process is also under development but the volume produced in this way is still low. This technique involves the use of a synthetic resin-based binder. Because affinity as well as compatibility for the polyester resins or epoxy resins used as matrix resins can be provided by selecting a synthetic resin-based binder (urethane resin emulsion, epoxy resin emulsion, water-soluble epoxy resin, etc.), the oil removal process becomes unnecessary. In the case of glass fiber, a great deal of energy has been expended on the development of primary sizing binders, which accounts for the lack of investigation into secondary sizing agents. There are no real problems as long as the primary sizing agent can prevent damage to the warps caused by a reed and a harness in weaving and can control fuzz, but in actuality, the process does not go all that smoothly, so a secondary sizing agent is generally used. This is the case even when the glass cloth is subjected to an oil removal process with heating. Furthermore, all synthetic resin-based binders are sticky and tend to produce defects such as streaks in the warps in weaving, even though the wefts remain unaffected.

[0004]

[Problems to be Solved by the Invention] The present invention proposes a solution to such problems by providing a warp secondary sizing agent for

glass fiber, which causes no warp fuzz when weaving glass cloth that requires no thermal oil removal process, produces cloth with a good appearance, and controls the development of surface fuzz on the cloth. Another object of the present invention is to provide a warp secondary sizing agent which does not adversely affect the properties of a laminate, such as solder heat resistance, even when a laminate, i.e., a final product, is made where the secondary sizing agent remains in the glass cloth, and to provide glass cloth using said sizing agent.

[0005]

[An Approach to Solving the Problems] The object of the invention is to solve the aforesaid problems by using a secondary sizing agent composed mainly of polyvinylpyrrolidone (hereinafter abbreviated as PVP) and that contains an additive such as a polyethylene oxide (hereinafter PEO) of high molecular weight for the warps of glass cloth. PVP products that can be used in the invention preferably have K-values of 15—120 (molecular weight = 10,000—1,450,000), and more preferably K-values of 30—90 (molecular weight = 40,000—630,000). When the K-values are lower than this, film formability is not as good and the warp protecting ability as a sizing agent decreases. When the K-values are higher than this, solubility in water decreases. In the secondary sizing agent of the invention, about 0.1—0.5% of a polyethylene oxide of high molecular weight, a water-soluble epoxy resin as a binding component, and a lubricating component or antistatic agent can be added as a film component in addition to PVP.

[0006] The secondary sizing agent of the invention is used as a mixed aqueous solution with an effective component content of 1—5%. The adhering rate on the warps is 1.0—4.0%, and preferably 1.0—2.0%. The secondary sizing

agent of the invention is compatible with matrix resins such as epoxy resins, and can provide good laminate properties such as solder heat resistance even without a thermal oil removal process, by using a synthetic resin-based binder such as mentioned earlier in the primary sizing. Furthermore, it can also be used as a secondary sizing agent for warps even in the case of starch-based primary binders of the type in general use today. In this latter case, there must be an oil removal process after weaving.

[0007]

[Actual Examples]

Actual Example 1

1. Spinning the Glass Fiber

(1) Glass Fiber .... ECE 225 1/0 1Z

(2) Binder Composition:

(a) Film Component .... Epikote 828 (Shell Chemical Co.) with 1 mole of diethanolamine added (2.0% as the effective component).

(b) Surface Treatment Agent .... γ-aminopropyltriethoxysilane (0.3% as the effective component).

(c) Lubricating Agent .... butyl stearate (0.5% as effective component).

(d) Water 97.2%

(3) Binder Adhering Rate 0.2%

2. Warp Sizing

The warp beam is prepared by applying a secondary sizing agent of the following composition to the glass yarn spun as specified in section 1.

PVP (K - 30) .... 1.5% (Wako Chemical Co., Ltd.)

PEO-3 .... 0.1% (Sumitomo Seika Co., Ltd.) (molecular weight 50,000-700,000).

Etheric nonionic active agent .... 0.05% (warp adhering rate = 1.53%).

Wefts of the glass yarn in section 1 were driven into warps coated with the secondary sizing agent as mentioned above, to carry out a weaving test. Table 2 shows the results of the weaving test. The loom used was an air jet type. Rotational speed = 400 rpm.

[0008]

3. Evaluation of the Woven Cloth

The cloth thus woven was tested with respect to impregnability with epoxy resin. In this test, a piece of the glass cloth 10-cm square was floated in epoxy resin varnish with an adjusted viscosity of 150 cps, then the time until the bubbles no longer emerged was measured. Table 3 shows the results. A laminate was prepared using the woven cloth and a solder heat resistance test was carried out.

(a) Preparation of a Laminate

• A prepreg was prepared using an FR-4 type epoxy resin varnish (resin content = 46%).

• Five pieces of prepregs were stacked on one another, copper foil 18 μm thick was placed on both sides, and the resulting assembly was bonded together with heat and pressure to prepare a laminate (thickness = 0.55 mm).

(b) Solder Heat Resistance Test

• The copper foil was removed by etching the laminate prepared as mentioned above with a ferric chloride solution, then the resulting product was

cut into 4 cm × 4 cm pieces to use as samples.

• The samples were treated at 133°C in a pressure cooker.

• Each sample thus treated was immersed in molten solder at 260°C for 20 seconds, then the sample was visually checked for the presence or absence of swelling.

Table 4 shows the results.

[0009]

Actual Example 2

The procedures followed were similar to those of Actual Example 1, except the amount of PVP added was adjusted to 2.0%. Warp adhering rate = 1.72%.

Actual Example 3

The procedures followed were similar to those of Actual Example 1, except the type of PVP was changed to K = 90 and the amount added was 1.0%. Warp adhering rate = 1.46%.

Actual Example 4

The procedures followed were similar to those of Actual Example 3, except the amount of PVP added was adjusted to 1.5%. Warp adhering rate = 1.64%.

[0010]

Comparison Example 1

The procedures followed were similar to those of the Actual Examples,

except the composition of the secondary sizing agent was as follows:

Starch (cornstarch) 1.2%

PVA (GL-05) 4.6%

Etheric nonionic active agent .... 0.08% (warp adhering rate = 4.63%)

Comparison Example 2

The cloth woven in Comparison Example 1 was heated at 500°C for 24 hours to remove the oil, then surface-treated with 0.7% of γ-aminopropyltriethoxysilane.

[0011] The results on Actual Examples 2-4 and Comparison Examples 1-2 are also shown in Tables 1-4. Table 1 shows the composition of the secondary sizing agents of the Actual Examples and Comparison Examples.

[0012]

[Table 1]

TABLE 1. KEY: (a) Actual Example; (b) Comparison Example; (c) nonionic active agent; (d) starch; and (e) cloth from Comparison Example 1 heated to remove the oil.

	(a) 実施例				(b) 比較例	
	1	2	3	4	1	2
PVP (K-30)	1.5	2.0	-	-	-	(e) 比較例1のクロスを加熱脱油したもの
PVP (K-90)	-	-	1.0	1.5	-	
PEO-3	0.1	0.1	0.1	0.1	-	
非イオン活性剤(c)	0.05	0.05	0.05	0.05	0.08	
澱粉 (d)	-	-	-	-	1.2	
PVA GL-05	-	-	-	-	4.6	

PVP (K = 30, K = 90): manufactured by Wako Chemical Co., Ltd.

PEO-3: manufactured by Sumitomo Chemical Co., Ltd. (molecular weight = 500,000-700,000)

PVA GL-05: manufactured by Nippon Gosei Co., Ltd.

[0013] Table 2 shows the weaving ability results for the Actual Examples and Comparison Examples. Weaving ability was evaluated in terms of the number of times the machine stopped in weaving 50 m, and the amount of surface fluff on the woven cloth.

[0014]

[Table 2]

TABLE 2. KEY: (a) Actual Example .... ; (b) Comparison Example 1; (c) weaving ability; (d) surface fuzz on glass cloth; (e) no machine stoppage (0 times/50 m); and (f) 0–4 pieces of fluff.

		製 織 性 (c)	ガラスクロスの表面毛羽 (d)
(a)	実施例1	停台無し（0回／50m）	0～4本 (f)
	実施例2	〃	〃
	実施例3	〃	〃
	実施例4	〃	〃
(b)	比較例1	〃	〃

(e)

[0015] Table 3 shows the impregnability measurement results for the glass cloth of the Actual Examples and Comparison Examples.

[0016]

[Table 3]

TABLE 3. KEY: (a) Actual Example .... ; (b) Comparison Example .... ; (c) impregnation time; and (d) not impregnated.

	含 浸 時 間 (c)
実施例1 (a)	12′ 00″
実施例2	13′ 30″
実施例3	13′ 00″
実施例4	13′ 30″
比較例1 (b)	含浸せず (d)
比較例2	14′ 30″

[0017] Table 4 shows the solder heat resistance results for laminates made with the glass cloth of the Actual Examples and Comparison Examples.

[0018]

[Table 4]

TABLE 4. KEY: (a) Actual Example .... ; (b) Comparison Example .... ; (c) time in the pressure cooker at 133°C; and (d) .... minutes.

	プレッシャークッカー時間 133℃ (c)		
	30分 (d)	45分 (d)	60分 (d)
実施例1 (a)	○○○	○○○	○○△
実施例2	○○○	○○△	○△×
実施例3	○○○	○○○	○○○
実施例4	○○○	○○△	○○×
比較例1 (b)	×××	×××	×××
比較例2	○○○	○○○	○△△

Evaluation criteria in Table 4 are as follows: (○) no swelling; (△) slight swelling; and (×) swelling.

[0019]

[Advantages of the Invention] The warp secondary sizing agents for glass fiber of the invention have weaving ability equivalent to that of a starch-based secondary sizing agent. They can also provide impregnability with mat-

rix resins and solder heat resistance for a formed laminate which are equivalent or better when compared with the case of using glass cloth subjected to the conventional oil removal treatment, using heat, even if glass cloth woven using this secondary sizing agent is used without removing the oil.